

Title	Amorphous Magnetism : its Overview
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Citation	物性研究 (1984), 42(1): A35-A45
Issue Date	1984-04-20
URL	http://hdl.handle.net/2433/91284
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Amorphous Magnetism; its Overview

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Magnetism in structurally amorphous alloys has become the subject of experimental and theoretical interest as a topic in solid state physics. The atomic states in these solids are inequivalent both structurally and magnetically. Because of this disordered structure, many interesting physical properties not observed in the corresponding crystalline magnets are just now becoming apparent. A number of review papers on the subject have appeared in recent years.

For many physicists, however, I think that the subject is not so familiar, since the materials have been mainly fabricated and studied by the workers in the field of material science. Accordingly, here, an overview of amorphous magnetism is given only by showing some interesting phenomena in the field. For the graduate student and experienced physicist who are looking into the field of amorphous magnetism for the first time, my book, Amorphous Magnetism, CRC Press INC, Boca Raton, U.S.A. (1984), may be suggested.

Introduction

At first we should note that "amorphous" and "disordered" do not mean the same thing. "Amorphous" refers to the lack of a crystalline lattice, which implies that amorphous magnets are disordered. But not all disordered magnets are amorphous. There are also disordered crystalline alloys. For comparison, a classification of disorder in magnetic systems is shown in Table 1.

Table 1. Disorder in Magnetic Systems

Systems	Atomic Positions	Spin Positions	Spin Magnitude	Exchange Interaction
Crystalline elements	Order	Order	Order	Order
Spin glass	Order	Disorder	Order	Disorder
Solid solution alloys	Order	Order	Disorder	Disorder
Solid solution compounds	Disorder	Order	Order	Disorder
Amorphous magnets	Disorder	Disorder	Disorder	Disorder

Thus, amorphous magnets constitute a class of systems with the highest level of disorder. Some characteristic behaviour observed in spin glasses and solid solution alloys are also observed in amorphous magnets.

In amorphous magnetic materials, although the long-range order for the distribution of magnetic atoms does not exist, a magnetic long-range order is possible, since its magnetism is determined by exchange interactions between neighbouring atoms and also randomly distributed local magnetic anisotropies. The atomic magnetic moments in amorphous magnets usually take one of the arrangements shown in Fig.1. Pure amorphous transition metals and amorphous transition metal-metalloid

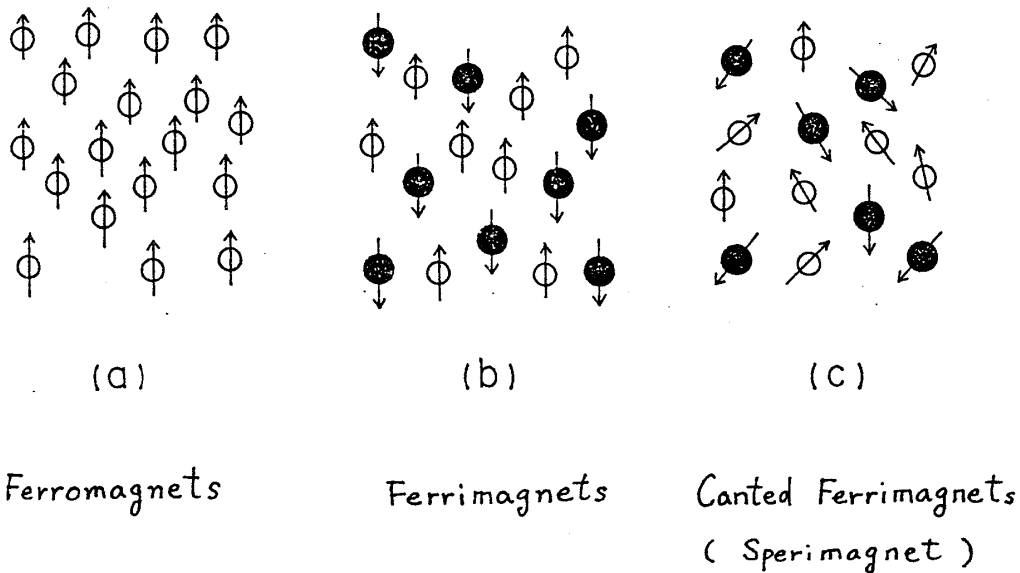


Fig. 1

alloys are reasonably well described as aligned ferromagnets as in Fig.1(a). The transition metal-heavy rare earth alloy systems are usually ferrimagnets, such as in Fig.1(b), with the rare earth moments (black circles) pointing oppositely to the transition metal moments (white circles) forming a two-subnetwork structure. The arrangement of Fig.1(c) is termed as a canted ferrimagnet (or a sperimagnet); and if the white circles are all replaced by black circles in Fig.1(c), it becomes a speromagnet or an asperomagnet.

One of characteristic features in amorphous magnets is that some of crystalline materials with an antiferromagnetic spin arrangement become ferromagnetic in the amorphous state, as shown in Table 2. In contrast with the case of crystalline magnets, antiferromagnetism may not be a suitable ordering phase in amorphous magnets. Spin glass like ordering with random spin orientations is generally observed instead of antiferromagnetism in amorphous magnets. The helical spin structure has not been observed in amorphous magnets.

Table 2

Comparison of Magnetic Properties in Crystalline(Cr)
and Amorphous (Am) states.

Substance	Spin Arrangement		Transition Temperatures	
	Cr	Am	Cr (T _N)	Am (T _c)
FeF ₂	ANT	F	78	21
FeCl ₂	ANT	F	24	21
FeBr ₂	ANT	F	11	21
Bi ₂ Fe ₄ O ₉	ANT	F	265	600
Gd ₅₄ Ag ₄₆	ANT	F	145	122
GdCu ₂	ANT	F	41	75
MnPt	ANT	F	—	—

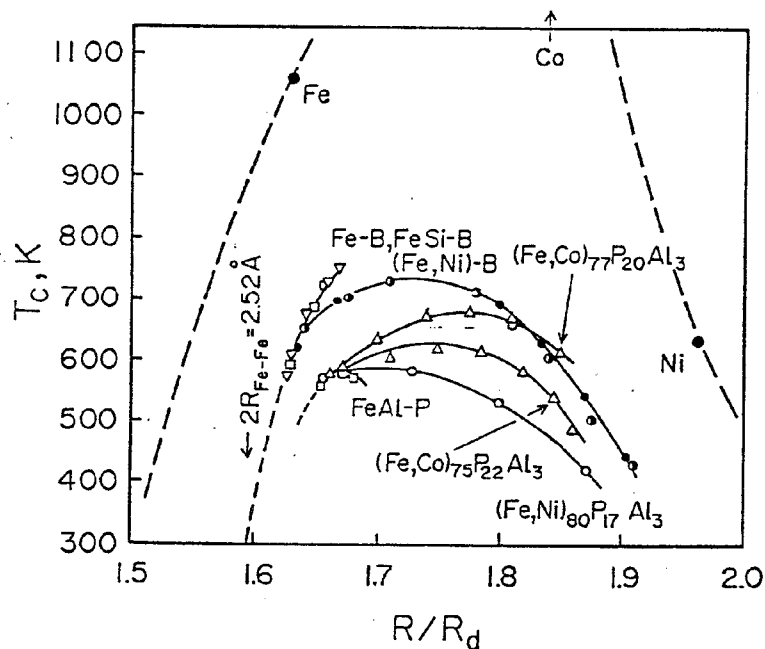
Transition Temperature

The Curie temperature, T_C, of an amorphous magnet is, on the molecular field approximation, given by

$$3kT_C = S(S+1) \int J(R)g(R)d^3R, \quad (1)$$

where S is the spin value and g(R) is for the pair correlation function of magnetic atoms. The existence of ferromagnetism in amorphous states is determined by the relative relation between the range of exchange interaction and the configuration of magnetic atoms. In equation (1), how should we take the form of exchange interaction as a function of the distance between atoms? One way may be to take the Bethe-Slater curve of direct exchange interaction in crystalline magnets. In Fig.2, the T_C values of different glasses are plotted in the function of R/R_d, where R_d is the radius of d-shell. The result may suggest indirectly the Bethe-Slater type curve for direct exchange interaction. On the other hand, the standard RKKY expression for indirect exchange coupling based on plane wave states may no longer hold, due to lack of long-range atomic ordering. At the present stage, lack of detailed knowledge of the electronic structure in amorphous magnets is a major stumbling block in understanding the definite form of the exchange interaction. However, because of a strong localization tendency of electrons in amorphous systems, as expected from the large residual resistivity, we may generally assume that a description by localized spins is a more valid starting point for the

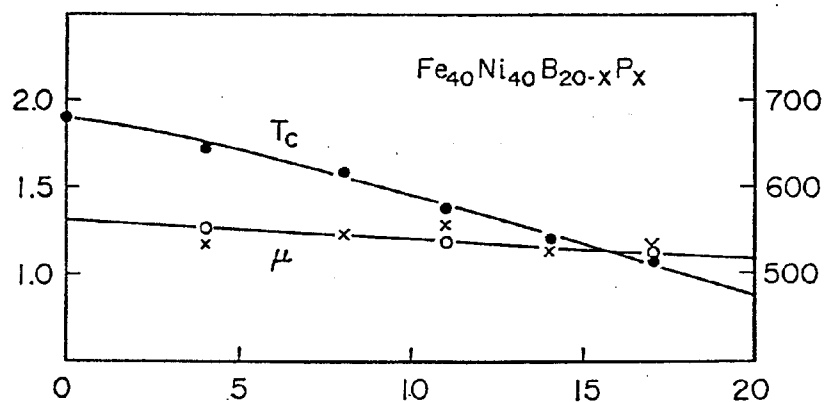
Fig. 2



theories of amorphous magnetic systems than for those of the corresponding crystalline systems.

In a number of metallic glasses, there is growing experimental evidence which suggests that nonmagnetic metalloid elements play a significant role in the magnetic properties of the alloys. An example is shown in Fig.3. Among other

Fig. 3



metallic glasses, amorphous Fe_xB_{100-x} alloys express some characteristic behaviours for the magnetic properties. The Curie temperature T_c rises as a function of increasing B concentration up to a maximum of 750K at about 30% B and then decreases, the magnetism disappearing at about 60% B, as in Fig.4. As indicated by Ichikawa, as far as coordination number and nearest-neighbour distance are concerned, amorphous pure Fe (in an unstable state) may be closer to a f.c.c.

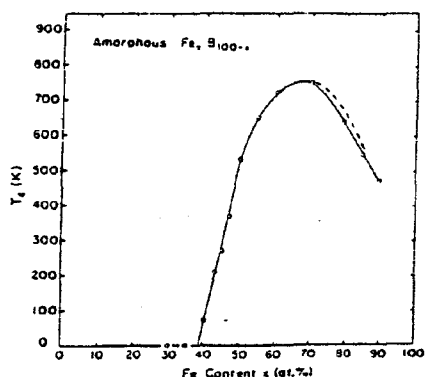
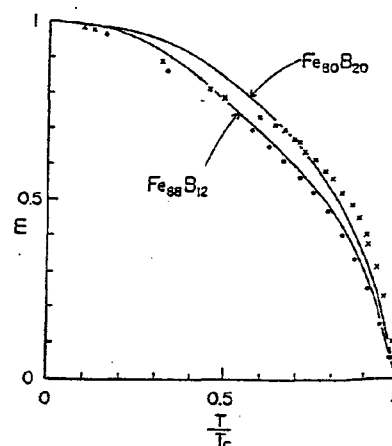


Fig. 4



structure than a b.c.c. structure. Accordingly, one may assume that the iron in a f.c.c. environment would have two magnetic states; Fe(I) states, strongly ferromagnetic and Fe(II) states antiferromagnetic. Experimentally, however, the Curie temperature for amorphous pure Fe seems to be near 200K. It is also known that amorphous $\text{Fe}_x\text{B}_{100-x}$ alloys exhibit the invar character. However, this systems show the resistivity minimum below the transition temperature, which phenomenon is generally observed in amorphous magnets.

Phase Diagram

The magnetic phase diagrams for three series of amorphous $(\text{A}_x\text{B}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ alloys, where (A,B) are (Fe,Ni), (Co,Ni), and (Fe,Mn), are shown in Fig.5.

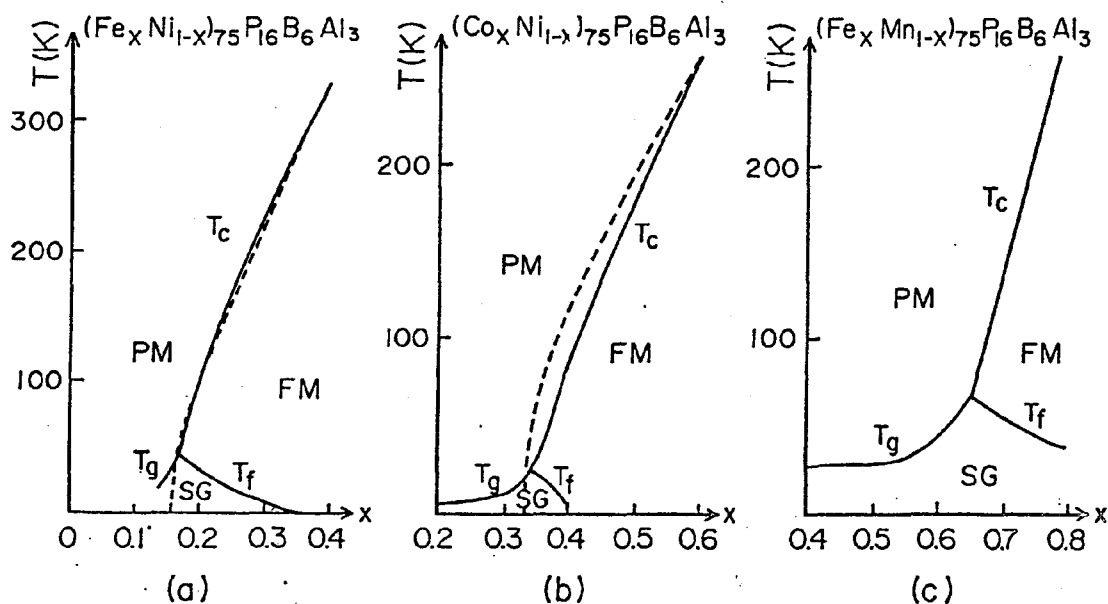


Fig.5

We can see paramagnet (PM) to ferromagnet

(FM) and ferromagnet (FM) to spin-glass (SG) transitions upon cooling. From a large number of observations, it is known that Ni atom is nonmagnetic, if the metalloid concentration is near 20%, such as $(\text{Fe}_x\text{Ni}_{1-x})_{80}\text{B}_{20}$. Structurally, to a first approximation metal-metalloid magnetic alloys with the composition being in the vicinity of 80 at % metal can be represented by a dense random packing (D.R.P.) of the metal atoms with larger spheres. Metalloid atoms with the smaller spheres occupy the Bernal holes which are inherent in the D.R.P.

Amorphous $\text{Y}_{1-x}\text{Fe}_x$ alloys are another interesting system. The spin structure evolves continuously from a speromagnetic one for YFe_2 to an asperomagnetic one with an increasing net moment as the Fe/Y ratio increases, as in Fig.6.

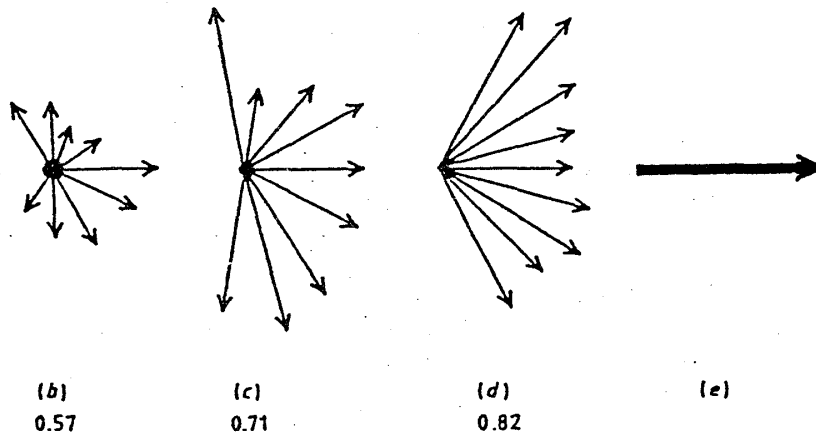


Figure 6 Schematic magnetic structures of (a)-(d) amorphous $\text{Y}_{1-x}\text{Fe}_x$ alloys with $x = 0.32, 0.57, 0.71, 0.82$ and (e) crystalline iron.

The noncollinear structures in these alloys is unlikely to have much to do with random single-ion anisotropy given by the Hamiltonian (2), but results from a broad distribution of exchange field.

For amorphous rare earth alloys with nonzero orbital angular momenta, one of the important consequences of topological disorder is to introduce randomly varying "crystal fields" at each atomic site because of the random local environments. The Hamiltonian is given by

$$\mathcal{H} = -\sum_i D_i (S_{z_i})^2 - \frac{1}{2} \sum_{i,j} J_{ij} \tilde{S}_i \cdot \tilde{S}_j, \quad (2)$$

where the local easy axes at each site, z_i , may vary randomly in direction. D_i is a positive value. Perhaps the most interesting question concerning the random local anisotropy model is the positive exchange. On this problem a number of workers have discussed by means of computer algorithms. It is now taking shape.

At the present time, it appears that the most theoretical works are concluding that the ground state is not the asperomagnetic state, particularly for large anisotropy values. A qualitative phase diagram for the random anisotropy model is shown in Fig.7. The dashed line in the figure indicates the possibility of a phase

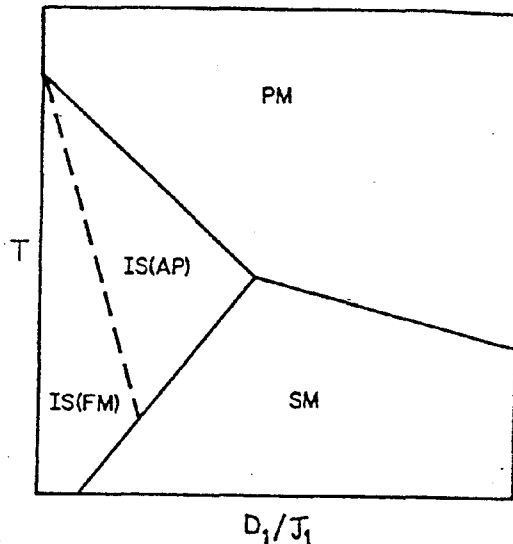


Fig. 7

Schematic phase diagram for a RMA system. The abbreviations are PM - paramagnetic; SM - speromagnetic; IS(AP) - Aharony and Pytte infinite susceptibility state; IS(FM) - infinite susceptibility ferromagnetic state with a domain structure.

boundary between an infinite susceptibility phase with no order (IS(AP)) and an infinite susceptibility phase with ferromagnetic domains (IS(FM)).

Spin Waves

Since amorphous magnetic materials constitute a class of systems with the highest level of disorder, one may have a question whether spin waves can be defined in amorphous ferromagnets or not; in such a system, so called "wave vectors" are not a good quantum number, and no simply defined Brillouin zone exists. One of the surprising facts found in amorphous ferromagnets is that the concept of magnons as noninteracting quasiparticles is valid until a rather high temperature region in contrast to that of crystalline case. That is to say, the Bloch's $T^{3/2}$ law is a general feature of amorphous ferromagnets

$$M(T) = M(0) [1 - BT^{\frac{3}{2}} - CT^{\frac{5}{2}} - \dots] , \quad (3)$$

with

$$B = 2.612 \frac{1}{M(0)} \left(\frac{k_B}{4\pi D} \right)^{\frac{3}{2}} , \quad (4)$$

where D is the spin-wave stiffness constant. In fact, magnetization measurements

and neutron diffraction show that the $T^{3/2}$ term dominates even to higher relative temperatures ($T/T_C \sim 0.4$) than crystalline materials ($T/T_C \sim 0.2$). The quantity of B in (3) is, by a factor of two to four, larger in amorphous ferromagnets than in related crystalline ferromagnets. The large value of B in amorphous ferromagnets means that the D value is small. The small D value may be interpreted as the softening of D originating from the "structural fluctuation" peculiar to amorphous magnets.

Following is another aspect of peculiar results in spin waves of amorphous ferromagnets. In some materials, discrepancies have been found between the B value obtained from the magnetization measurements and the B_{sw} value calculated from (4) in terms of D_{sw} determined by neutron scattering. That is, the value of B_{sw} is smaller, by as much as a factor of two, than the value obtained by the other technique. Therefore, several arguments have been put forward to clarify such a discrepancy. However, possibly a solution of the discrepancy may come from the observation of Ishikawa et al. that as shown in Table 3 the disagreement between

Spin wave stiffnesses (D_{sw} and D_{mag}) of various amorphous alloys,

Table 3

Compounds	T_C (K)	D_{sw}	D_{mag}	D_{sw}/D_{mag}	Remarks
					BS
$Fe_{80}B_{20}$	647*	170±25	92±7	1.8±0.3	IV
$Fe_{75}P_{16}B_6Al_3$	630±12	134±5	117±10	1.14±0.15	IV?
Co_4P	620	185	116	1.60	
		135±5		1.17±0.05	SR
$Fe_{75}P_{15}Co_{10}$	597*	135*	116	1.29	IV
		125±25*		1.03±0.2	
$(Fe_{65}Ni_{35})_{75}P_{16}B_6Al_3$	576±6	114±10	115±3	1.0±0.1	no IV
$Fe_{96}B_{14}$	570	118±6	68.5±1.5	1.7±0.15	IV
$(Fe_{50}Ni_{50})_{75}P_{16}B_6Al_3$	482±6	91±3	94±10	1.0±0.1	no IV
$(Fe_{93}Mo_7)_{80}P_{10}$	450	85	67	1.27	small IV
$Fe_{70}Cr_{10}P_{13}C_7$	360	60±2	54±2	1.1±0.1	no IV
$(Fe_{30}Ni_{70})_{75}P_{16}B_6Al_3$	258±3	36±2	61±10	0.59±2	
Crystalline					
$Fe_{65}Ni_{35}$	500±3	142±5	59	2.4±0.1	IV
Fe_3Pt	435±2	78±5	60	1.3±0.1	IV

IV ; The sample shows the Invar effect

BS ; D_{sw} was determined by Brillouin scattering

SR ; D_{sw} was determined by spin wave resonance

* T_C values and D_{sw} are different from those of table 4.1 and table 4.3, which difference depends on samples and workers.

D_{sw} and D_{mag} (D_{mag} is obtained in terms of (4) from the magnetization measurements) in some amorphous ferromagnets is a characteristic of the spin dynamics of Invar alloys.

Very recently, an anomalous behaviour of the spin-wave stiffness constant is found in a few amorphous ferromagnets; the spin-wave stiffness constant D , determined from $M - T^{3/2}$ plots, increases with increasing external field H . An example is shown in Fig.8. As discussed by Kaneyoshi, Phys. Stat. Sol. (b) 118 (1983) 751,

Cr (x)	μ (μ_B) 0 K	B (K ^{3/2}) (10^{-6})	D meV.Å ²	D/T_c
0	0,994	29	115	0,20
1	0,941	27	115	0,21
3	0,824	43	100	0,21
4	0,772	49	95	0,21
5	0,720	57	90	0,21

Some magnetic parameters versus Cr concentration (x) in :

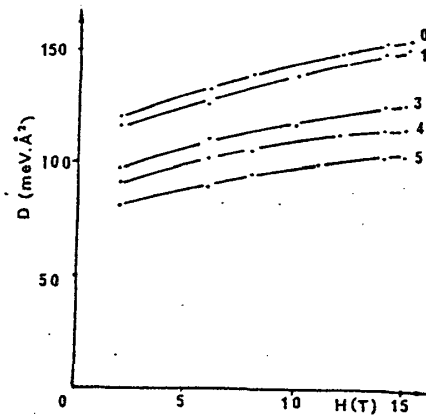
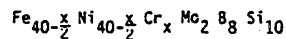


Fig. 8

- Experimental field dependence of D of different Cr composition.
The number indicate Cr concentration.

the characteristic may be a general phenomenon for amorphous ferromagnetic alloys as well as for crystalline ferromagnets with a heterogeneous distribution of magnetic moments.

Critical Phenomena

A crystalline ferromagnet exhibits a sharp phase transition, where many physical properties, like the specific heat or magnetic susceptibility, are divergent. In an amorphous system, on the other hand, there exist both structural and compositional randomness. Accordingly, one may expect a "smearing" of the transition in an amorphous ferromagnet. Experimentally, however, many amorphous ferromagnetic alloys are observed to undergo sharp transitions into their ordered state. From these experimental results, Mizoguchi has suggested that an amorphous alloy may behave as an ideal isotropic ferromagnet in the critical region, because the fluctuation of magnetization becomes long-range and such the microscopic randomness is averaged out. Now, there have been considerable efforts directed at

describing the critical behaviour of such amorphous ferromagnets in terms of the usual critical indices, β , γ , δ , and α , defined by

$$M(0, T) \propto (-t)^\beta \quad \text{for } T < T_C$$

$$\chi(0, T) \propto t^{-\gamma} \quad \text{for } T > T_C$$

$$M(H, T_C) \propto H^{1/\delta} \quad \text{at } T = T_C$$

$$C \propto t^{-\alpha} \quad \text{for } T > T_C$$

$$\propto t^{-\alpha'} \quad \text{for } T < T_C,$$

where

$$t = \frac{T - T_C}{T_C}.$$

In Table 4, the observed critical exponent values of amorphous ferromagnets are collected.

Critical Indices of Amorphous Ferromagnets

Substances	T_C (K)	β	γ	δ	α	Reference
$\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (Metglas 2826)	519.9 (± 0.2)	0.38 (± 0.01)	1.31 (± 0.02)	4.46 (± 0.04)	-0.07* (± 0.04)	85
$\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ (Metglas 2826A)	249 (± 0.1)	0.42 (± 0.04)	1.35 (± 0.05)	4.3 (± 0.1)	-0.19* (± 0.13)	136
		0.41 (± 0.02)	1.67 (± 0.08)	5.07 (± 0.05)	-0.49* (± 0.12)	137
$\text{Fe}_{29}\text{Ni}_{49}\text{P}_{14}\text{B}_6\text{Si}_2$ (Metglas 21268)	384.5 (± 0.01)	0.40 (± 0.01)	1.7 (± 0.1)	5.25 (± 0.10)	-0.50* (± 0.12)	138
$\text{Fe}_{10}\text{Ni}_{70}\text{B}_{19}\text{Si}_1$	186.5 (± 0.3)	0.42 (± 0.02)	1.35 (± 0.04)	4.49 (± 0.05)	-0.19* (± 0.08)	139
$\text{Fe}_{13}\text{Ni}_{67}\text{B}_{19}\text{Si}_1$	268.5 (± 0.2)	0.42 (± 0.02)	1.35 (± 0.04)	4.45 (± 0.05)	-0.19* (± 0.08)	140
$\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$	227.7 (± 0.5)	0.39 (± 0.02)	1.33 (± 0.05)	4.45 (± 0.07)	-0.11* (± 0.09)	141
$(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{16}\text{B}_{16}\text{Al}_3$ x = 0.4		0.39 (± 0.02)	1.58* (± 0.10)	5.05 (± 0.15)	-0.36* (± 0.12)	142
x = 0.8		0.38 (± 0.02)	1.55* (± 0.10)	5.08 (± 0.15)	-0.31* (± 0.12)	
$\text{Fe}_{80}\text{P}_{13}\text{C}_7$	586.55 (± 0.10)	0.38 (± 0.02)	1.30 (± 0.05)	4.47 (± 0.05)	-0.06* (± 0.09)	143
	585.9 (± 0.4)	0.36 (± 0.02)				144
$\text{Co}_{70}\text{B}_{20}\text{P}_{10}$	453.01 (± 0.07)	0.410 (± 0.006)	1.303 (± 0.012)	4.203 (± 0.002)	-0.14* (± 0.05)	135
$\text{Ga}_{80}\text{Al}_{20}$	149.45 (± 0.2)	0.44 (± 0.02)	1.29 (± 0.05)	3.96 (± 0.03)	-0.17* (± 0.09)	145
$\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$					-0.18 (± 0.04)	146
d=3 crystalline		0.33	1.36 ($s=\frac{1}{2}$)			
Heisenberg		- 0.37	(± 0.04)			
ferromagnet			1.33 ($s=\infty$) (± 0.01)*	4.2		

* calculated values from the scaling relations

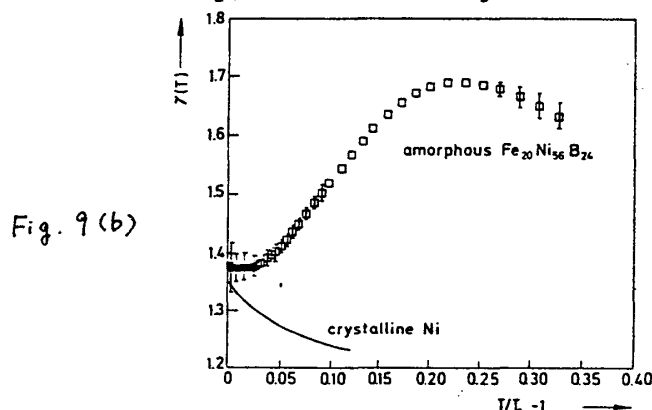
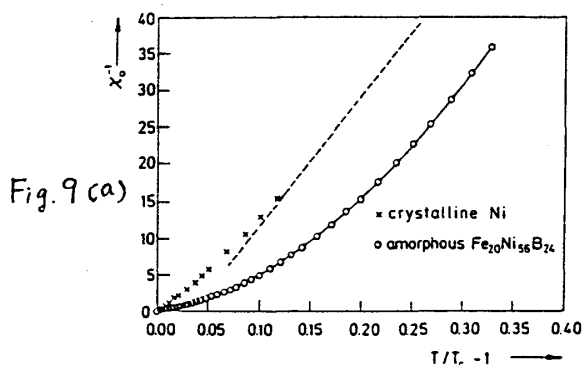
Table 4

Now, one can test whether the scaling law hypothesis is valid in amorphous ferromagnets, in terms of the observed values of the critical exponents β , γ , and δ . Then, we find that the static scaling law are fairly well valid. The experimental data also present a systematic trend; all the critical exponents other than β seem to possess values, although scattered, close to their crystalline values, and follow the predictions of a three-dimensional Heisenberg model. On the other hand, the value of the exponent β is slightly enhanced in comparison with its crystalline value and tends in common to be close to 0.4 rather than to the highest estimated value $\beta \approx 0.37$ of the Heisenberg model.

One prominent difference between the amorphous and crystalline ferromagnets concerns the temperature dependence of the susceptibility beyond the critical region; the large downward curvature of the inverse paramagnetic susceptibility are temptingly ascribed as a characteristic of highly disordered systems. In Fig.9(a), the temperature dependences of the inverse paramagnetic susceptibility of crystalline Ni and amorphous ferromagnetic $\text{Fe}_{20}\text{Ni}_{56}\text{B}_{24}$ are shown for comparison. In general, the transition region to the Curie-Weiss law extends over 100 ~ 200K in amorphous ferromagnets, whereas in the case of crystals this transition takes place within a temperature range of $\sim \frac{T_C}{25}$. For many amorphous ferromagnets, therefore, the effective exponent $\gamma(T)$ above T_C defined by

$$\gamma(T) = (T - T_C) \chi_{\text{para}}^{-1} \frac{d\chi_{\text{para}}}{dT}$$

Initially increases with temperature and then decreases to a mean field value $\gamma=1$, in contrast with crystalline ferromagnets showing a continuous decrease in $\gamma(T)$ from the value at $T=T_C$ towards a high-temperature value of unity, as shown in Fig.9(b).



In this short report of the meeting on the random spin systems, I showed only a few characteristic phenomena observed in amorphous magnets. Some of them have explained theoretically and others are left as open questions. Finally, amorphous magnetism is now a very large subject, in which a large number of interesting phenomena are found and many physicists are invited to solve the open questions.